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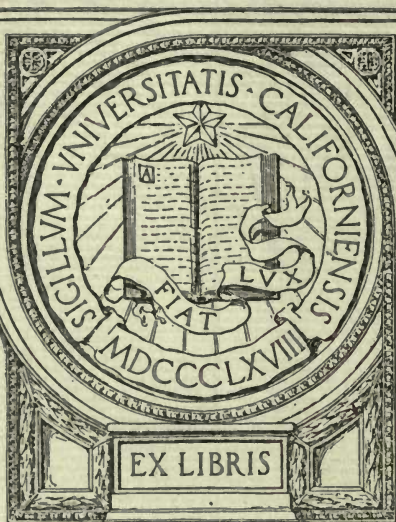
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OBSERVATIONS ON THE RARE EARTHS:
THE ULTRA-VIOLET ARC SPECTRUM
OF YTTRIUM

BY

LEONARD FRANCIS YNTEMA

A. B. Hope College, 1915

A. M. University of Illinois, 1917

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE

DEGREE OF

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

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to the
Anderson

ACKNOWLEDGMENT

The author wishes to express his appreciation of the help and encouragement given by Professor B. S. Hopkins, who suggested this problem and under whose direction the work was done.

OBSERVATIONS ON THE RARE EARTHS, XI: THE ARC SPECTRUM OF YTTRIUM¹

BY

L. F. YNTEMA WITH B. S. HOPKINS

During the progress of the work on the rare earth group of elements at the University of Illinois, several members of the group have been separated in a high state of purity and their atomic weights determined. This present investigation is a part of a plan that comprises the spectroscopic examination of a number of those elements in order to establish standards of purity that can be employed in future work on the separation of the members of the group.

The emission spectrum of yttrium has been studied by a number of workers. Values have been published by Kayser,² Eberhard,³ and Exner and Haschek.⁴ The latest, and probably the best determinations are those of Eder,⁵ which were made on yttrium material prepared by Auer v. Welsbach. They are included in the following table.

The yttrium examined was a portion of that prepared by the one of us and co-workers for the determination of the atomic weight value that has lately been accepted by the International Committee on Atomic Weights.⁶ The only known impurity was 0.005 per cent or less of holmium,—an estimate made by comparing the intensity of the absorption spectrum with standard solutions.

The spectrograph used is an autocollimating quartz prism machine constructed by Adam Hilger of London. Its dispersion increases from 17.5 angstroms per millimeter at 4500A° to 1.5 angstroms per millimeter at 2200 A°.

¹ Submitted by L. F. Yntema to the Graduate School of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Contribution from the Chemical Laboratory of the University of Illinois.

² Königl. preuss. Akad. d. Wiss., Berlin, 1903.

³ Zeitschr. f. wiss. Photogr., 7, p. 245, 1909.

⁴ "Die Spektren der Elemente bei normalem Druck, II," Leipzig und Wien, 1911.

⁵ Sitzber. K. Akad. wiss., Wien, IIa, 125, p. 471.

⁶ J. Amer. Chem. Soc., 42, p. 327, 1920; *Ibid.*, 41, p. 718, 1919. *Ibid.*, 38, p. 2332, 1916.

The iron spectrum was employed as reference.⁷ A bar of pure iron for this purpose was kindly furnished by the Westinghouse Electric and Manufacturing Company of East Pittsburg, Pennsylvania. Copper electrodes, as carriers for the yttrium oxide, were found to be preferable to the graphite generally employed, because the copper arc is steadier and the electrodes do not burn away as rapidly. Furthermore, a regulus of yttrium oxide in the molten copper is formed and mechanical loss is avoided.⁸

A direct current of four or five amperes at an E.M.F. of 220 volts was used.⁹

Seed plates, No. 23, size 4" by 10", were used and hydrochinone was used as a developer. The negative plates were measured on a dividing engine, made by Adam Hilger of London, which is graduated to read to 0.001 millimeter.

The wave-lengths in International Angstrom units, were calculated by Hartmann's dispersion formula.¹⁰

$$\lambda = \lambda^0 \frac{C}{R - R_0}$$

The mean of the determinations from at least four plates was taken.

The results are given in the following table. The first column gives the wave-lengths as measured in International Angstroms. The second column indicates the intensity and character of each line, the most prominent lines being assigned an intensity "10" and the faintest lines an intensity "1." The character or appearance of a line is indicated by letters that have the following significance:

d = diffuse

v = shaded to violet

R = reversed

BR = head of a band toward red

The column headed "Notes" contains other elements having lines that coincide closely with yttrium lines of lower order of

⁷ Handbuch der Spectroscopie, VI. Band, H. Kayser.

⁸ Pfund, *Astrophys. Jour.* 27, p. 296, 1908.

⁹ *Astrophys. Jour.* 39, p. 93, 1914.

¹⁰ *Astrophys. Jour.* 8, p. 218, 1898.

intensity. These elements were probably present as impurities in the material examined.

Intensity and Character of Spectral Lines of Yttrium

Yntema and Hopkins	I	Eder	I	Notes
.....	2231.55	1
2243.02	4	2243.03	2
.....	2328.95	1
2331.67	2	2331.63	1
2332.59	3	2332.58	2
2340.80	1	2340.79	1
2343.55	3d
2349.71	2	2349.69	1
2354.21	4	2354.20	3
2355.42	2	2355.40	1
2358.75	2	2358.70	2
2361.82	2	2361.81	2
2373.86	4
2385.24	5	2385.24	2
2398.10	2	2398.06	2
2404.09	1	2404.11	1
2413.94	3	2413.94	1
2417.29	2	2417.29	1
2422.19	7	2422.20	4
.....	2457.93	$\frac{1}{2}$
2460.13	2	2460.11	1
2460.60	3	2460.60	2
2465.80	2
.....	2479.09	1
.....	2479.80	1
2490.44	3
2492.68	1d
2516.13	2	Silicon
.....	2529.14	1
2540.31	3d	2540.28	1
2545.61	2d
2547.57	4	2547.56	2
2550.17	2d	2550.35	1
.....	2554.87	1
.....	2570.72	1
.....	2579.36	1
.....	2593.76	1
2594.89	2d	2594.88	1
2612.42	1d	2612.38	1
.....	2619.46	1
2634.36	1	2634.32	1

Yntema and Hopkins	I	Eder	I	Notes
2647.76	1(?)	2647.74	$\frac{1}{2}$
.....	2671.20	$\frac{1}{2}$
2672.09	3	2672.08	1
2681.67	3	2681.65	1
2684.20	1	2684.20	$\frac{1}{2}$
2694.18	4	2694.21	1
2695.37	3	2695.40	1
2699.01	2
2705.87	2	2705.85	1
2710.15	1(?)	2710.15	1
2720.04	2d	2719.99	1
2723.01	4	2723.00	3
2730.09	3	2730.06	1
.....	2733.93	1
2734.82	2	2734.85	2
2742.48	5	2742.55	3
.....	2749.23	1
2750.17	2	2750.20	2
.....	2755.79	1
.....	2756.33	1
2760.08	5	2760.10	3
2772.28	1
(2779.85)	1	Magnesium
2785.18	2	2785.19	2
2785.59	2	2785.58	2
2790.13	1
2791.23	2	2791.20	1
(2795.56)	2	(2795.53)	2	Magnesium
2800.10	3	2800.12	2
2801.14	1(?)
.....	(2802.73)	2	Magnesium
2807.77	1	2807.66	1
2813.65	3	2813.66	1
2818.87	2	2818.87	1
2822.57	2	2822.56	1
.....	2823.55	1
.....	2824.48	1
2826.33	2
2834.42	1	2834.39	1
2835.78	1d
2840.83	2	2840.84	1
2842.44	1
2842.63	1d
2850.63	1
.....	(2852.11)	2	Magnesium
2854.42	3	2854.42	2

Yntema and Hopkins	I	Eder	I	Notes
2856.30	2	2856.30	2
2857.91	1	2857.87	1
2871.23	1	2871.20	1
2873.29	1		
2881.60	1	(2881.60)	3	Silicon
2886.48	4	2886.49	2
2890.38	2	2890.40	1
		2891.32	1
2897.68	2	2897.68	1
2898.81	1	2898.82	1
2901.46	2d	2901.48	1
2919.06	6	2919.06	3
		2929.00	1
2930.00	2	2930.03	2
2930.75	1	2930.77	1
		2935.91	1
		2943.58	1
2948.41	8	2948.40	4
		2948.78	1
2953.13	1	2953.14	1
2955.86	1	2955.86	1
2964.97	7	2964.95	3
2973.89	1(?)	2973.91	1
2974.60	10	2974.60	4
		2977.99	1
2980.56	2	2980.55	2
2984.26	10	2984.25	4
2995.27	3	2995.25	2
		2996.94	3
3005.26	3	3005.25	2
		3009.51	1
3018.96	3d	3018.95	2
3021.73	3	3021.73	3
3022.28	3	3022.27	3
3023.73	1d	3023.70	1
3023.95	1d(?)	3023.99	1
		3027.68	1
		3030.08	1
		3036.59	3
		3037.82	1
3038.44	1	3038.46	1
		3039.98	1
3044.84	2	3044.84	2
3045.37	4		
3047.13	1	3047.11	1
3047.36	2	3047.41	1

Yntema and Hopkins	I	Eder	I	Notes
3049.88	1	3049.86	1
.....	3051.52	1
3053.25	1(?)	3053.26	2
3054.49	3(?)	3054.41	1
3055.22	3	3055.21	3
(3056.33)	1	(3056.33)	1	Sodium
(3059.52)	2	(3059.50)	2	Dysprosium?
.....	3065.83	1
.....	3067.27	1
3069.10	1(?)	3069.04	1
3072.37	2	3072.32	2
3076.49	2	3076.49	2
3077.00	1(?)	3076.95	1
3078.57	1d(?)	3078.57	1
3080.29	1
.....	(3082.16)	1	Aluminium
3086.88	3	3086.84	4
3091.74	3d	3091.70	3
.....	(3092.71)	3	Aluminium
.....	3093.75	3
.....	3095.49	1
3095.89	3	3095.88	4
3096.61	1d	3096.57	1
3103.29	1(?)	3103.25	1	Dysprosium?
3103.72	1	3103.69	2
3104.69	1	3104.69	2
.....	3108.86	2
.....	3109.77	1	Dysprosium?
.....	3110.50	1
3111.79	3	3111.80	3
3112.03	3	3112.03	3
3114.29	2	3114.27	3
.....	3118.50	1	Holmium?
.....	3122.60	1
.....	3126.00	1
.....	3128.74	3
3129.96	3	3129.93	4
.....	3133.15	1
3135.19	4	3135.16	4
.....	3140.63	1	Dyspro- sium?
.....	3141.16	1	Aldebaran- ium?
.....	3144.20	1
3152.68	2d-	3152.67	2
3155.66	1

Yntema and Hopkins	I	Eder	I	Notes
.....	3157.50	1
.....	3158.36	1
.....	(3158.88)	1	Calcium
.....	3159.47	1
.....	3160.54	1	Dyspro- sium?
.....	3162.83	1	Dyspro- sium?
.....	3164.76	1
.....	3170.00	1	Dyspro- sium?
3171.72	3	3171.69	2
3173.05	3	3173.05	4
.....	3173.72	1
.....	3174.36	1
3179.45	4	3179.40	4
3182.27	1	3182.23	2
3185.99	1	3185.93	1
.....	3188.75	1
3191.38	3	3191.29	3
.....	3193.29	2
.....	3194.37	2
3195.66	8	3195.61	6
.....	3197.69	1
3198.45	1(?)	3198.41	2
3200.29	10	3200.25	6
3203.37	10	3203.32	6
.....	3203.82	1
.....	3206.22	1
.....	3209.35	2
.....	3211.26	1
3212.24	1d	3212.28	2
.....	3214.04	1
.....	3215.20	1	Dyspro- sium?
.....	•
3216.68	10	3216.67	10
.....	3217.80	1
.....	3220.72	1
.....	3221.50	1	Dyspro- sium?
.....	3222.02	1
.....	3223.28	1	Dyspro- sium?
.....	3225.03	3
.....	3227.08	1
.....	3227.69	1

Yntema and Hopkins	I	Eder	I	Notes
.....	3230.57	2	Holmium
.....	3231.32	1
.....	3231.80	2
.....	3235.88	1	Dysprosium
.....	3237.93	1
.....	3239.29	1
3242.28	8	3242.28	15
.....	3245.07	1	Dysprosium
.....	3247.02	1
.....	3247.54	4	Copper
.....	3251.29	2	Dyspro- sium?
3252.34	2(?)	3252.27	3
.....	3255.82	1
.....	3256.20	1
.....	3257.52	1
.....	3261.23	1
3262.39	2
.....	3263.22	1
.....	3264.77	3	Holmium?
.....	3267.24	1
.....	3267.81	1
.....	3269.11	1
.....	3269.40	1
.....	3270.94	1
.....	3271.13	1
.....	3273.04	1
.....	3273.96	3	Copper?
.....	3275.56	2
.....	3278.43	2
.....	3279.35	1	Erbium?
.....	3280.13	2	Dyspro- sium?
.....	3280.91	4
.....	3281.98	1	Holmium?
.....	3282.45	3
.....	3282.77	1
.....	3283.21	2
.....	3283.85	1
.....	3286.68	3
3287.25	1	3287.21	3
.....	3287.93	1	Dyspro- sium?
.....	3289.37	3	Aldebaran- ium
.....	3290.11	1

Yntema and Hopkins	I	Eder	I	Notes
.....	3290.56	3
.....	3290.96	1	Holmium?
.....	3291.44	1	Dyspro- sium?
.....	3293.44	2
.....	3293.68	2
.....	3294.55	1
.....	3298.26	1
.....	3302.17	2
.....	3302.56	$\frac{1}{2}$
.....	3303.86	1
.....	3304.32	$\frac{1}{2}$
.....	3305.49	$\frac{1}{2}$
.....	3305.90	$\frac{1}{2}$
.....	3306.27	$\frac{1}{2}$
.....	3307.61	$\frac{1}{2}$
.....	3308.47	3
.....	3308.84	1
.....	3310.13	$\frac{1}{2}$
.....	3312.40	1
.....	3312.67	$\frac{1}{2}$
.....	3315.40	$\frac{1}{2}$
.....	3316.32	$\frac{1}{2}$
.....	3317.03	$\frac{1}{2}$
.....	3318.52	2
.....	3319.76	3
.....	3320.60	1
.....	3323.18	1
3327.97	10	3327.89	15
3330.90	2	3330.88	2
.....	3333.42	1
.....	3335.20	2
.....	3336.18	1
.....	3337.82	2
.....	3338.76	1
3340.36	2	3340.37	3
.....	3340.98	$\frac{1}{2}$
.....	3341.85	1
3344.51	1d	3344.53	2
.....	3349.26	1
.....	3352.64	$\frac{1}{2}$
.....	3353.56	$\frac{1}{2}$
.....	3354.57	2
3358.98	2	3358.94	2
3362.05	5	3361.99	5
.....	3364.79	2

Yntema and Hopkins		Eder	I	Notes
(3372.77)	2	Holmium
3377.76	2	3377.72	2
3379.85	1
3382.85	6	3382.83	$\frac{1}{2}$
.....	3383.06	1
3388.60	3	3388.58	2
3389.90	2d
3393.50	1(?)
3394.98	1
3397.05	3	3397.03	3
3399.02	2
3406.11	1
(3407.76)	1	Dysprosium
3409.72	1d
3412.49	2d	3412.47	2
3424.14	2d
(3429.15)	1d	Holmium
3431.00	2
3431.67	2d
.....	3433.02	1
3437.98	2d
(3445.52)	1d	Dysprosium
3448.85	5	3448.81	4
3450.88	2	3450.94	2
3453.03	1d	Holmium
3456.01	2d	Holmium
3461.01	2
3467.86	4	3467.88	4
3469.36	1
3470.14	1
3473.12	2
3474.28	1
.....	3484.06	2
3485.75	4	3485.73	4
3496.06	9	3496.09	8
3497.23	1
3498.93	2dv
3500.63	1d
3501.96	1
3503.47	1d
3506.51	2
3507.95	1
3510.54	1d
3511.19	1d	3511.20	3
3521.52	2d
.....	3512.90	2

Yntema and Hopkins	I	Eder	I	Notes
(3538.49)	1d	3531.65	2	Dysprosium
		3544.03	4	
		3544.93	3 [*]	
3545.94	1		6	Holmium?
3548.98	10	3548.99		
3551.76	1			
3552.71	5	3552.69	4	
3558.72	4			
3562.74	1d			
3564.00	1			
3571.42	3	3571.44	1	
3576.05	4	3576.04	2	
3584.43	7	3584.51	4	
3587.76	3	3587.75	1	
3589.61	2			
3592.85	7	3592.91	4	
3600.69	6	3600.72	6	
3601.92	6BR	3601.91	5	
		3608.84	1	
3611.05	8BR	3611.05	10	
3612.32	2			
3616.62	1			
		3618.77	1	
3620.93	6BR	3620.94	6	
3628.69	7BR	3628.70	5	
3633.01	10BR	3633.11	8	
		3635.32	1	
		3639.27	3	
3664.62	10BR	3664.59	10	
3668.51	2	3668.48	3	
3692.54	3	3692.54	6	
		3694.20	3	Aldebaran- ium
3696.62	1			
3710.14	10	3710.30	15	
		3716.94	1	
3718.10	2	3718.14	3	
		3724.76	2	
3732.19	1			
3738.60	2	3738.62	2	
3747.59	6BR	3747.55	3	
3749.90	2			
3755.50	1			
(3757.27)	1			Holmium
3760.02	1d			

Yntema and Hopkins	I	Eder		Notes
3761.45	1	Erbium
3762.18	1
3769.51	1
3770.38	2d
3774.28	10BR	3774.33	5
3776.53	6BR
3782.26	1
3788.62	10BR	3788.69	5
(3796.65)	1	Holmium
(3810.72)	1	Holmium
3818.32	6BR	3818.37	3
.....	3825.91	1
3832.84	10BR	3832.87	2
3836.79	1d
.....	3840.43	1 } *
3843.43	1d	}
3847.87	3v
(3872.12)	1	Dysprosium
3876.82	2
3878.31	4	3878.27	1
3884.81	1
3887.81	2	3887.93	2
.....	3890.13	1
3890.95	1d
3892.39	1	3892.41	2
.....	3900.27	1
3904.56	2	3904.59	2
3913.66	1
3918.30	2
3930.66	4	3930.65	3
3942.53	1d	Dyspro- sium?
3944.74	1	Dyspro- sium?
3946.20	1	3946.20	2
3946.95	1(?)
3950.36	10BR	3950.35	5
.....	3951.60	3
3955.05	2	3955.09	3
3967.72	1
3973.53	1d(?)	3973.45	2
3982.61	10	3982.60	8
3987.48	1	3987.50	1
(4000.54)	1(?)	(4000.44)	3	Holmium
(4008.00)	1	Erbium
4029.85	1	4029.86	1

Yntema and Hopkins	I	Eder	I	Notes
4039.80	5	4030.83	5}*	
4047.69	7	4047.65	6	
4049.45	1(?)			
(4053.93)	1dv			Holmium
		4065.02	1	
		4076.39	8}+	
4077.38	10			
4079.14	1(?)			
		4080.93	1	
4081.19	2d	4081.23	1	
4083.74	7	4083.71	5	
4085.50	1			
4090.45	1			
4095.45	1d			
4099.30	1			
4099.85	1			
4102.35	10BR	4102.38	10	
4106.41	2	4106.39	1	
4110.82	2	4110.81	2	
4124.96	4			
		4125.93	5}*	
4128.25	10BR	4128.32	10	
4142.89	9BR	4142.87	10	
4157.63	3	4157.63	2	
(4163.10)	1d			Holmium
4167.56	8	4167.52	8	
4169.42	1(?)			
4174.16	7	4174.14	4	
4177.54	10BR	4177.51	5	
(4186.83)	1d			Dysprosium
4191.26	1d(?)			
4199.26	3	4199.28	3	

* The values given by Kayser and others agree with those found by the authors. It is suggested that the discrepancies may be due to clerical errors.

The impurities found to be present in the yttrium material were the rare earth elements, holmium, erbium, and dysprosium, besides magnesium, and silicon. The presence of the rare earths is to be expected in small amounts. The order of increasing solubility of the bromates, which were used for the first step in the purification of the yttrium, is as follows:—

Dy, Ho, Y, Er

The final purification was accomplished by methods depending on differences in basicity. The order of decreasing basicity is as follows:—

Y, Dy, Ho, Er

Complete separation of yttrium from its less basic neighbors is hardly possible, but the separation was so nearly complete that their most prominent lines were found to be of the faintest order in the spectrograms obtained.

The solution, from which the yttrium was precipitated as oxalate, had stood in Jena glass for some time; the silicon and possibly the magnesium were introduced by solution of the glass.

Attention may be called to the fact that the yttrium material examined has a few lines in common with the eurosamarium of Eder.¹¹ Lines 4309.65 \AA , 4174.16 \AA , and 3950.35 \AA are prominent yttrium lines and they are reported as faint lines of eurosamarium. Other prominent yttrium lines, however, were not found by Eder in eurosamarium. There are several instances of coincidence of rather faint lines, such as those at 4090.45 \AA and 3129.96 \AA , but these are probably accidental. It must be concluded that Eder's material contained no more than a very small per cent of yttrium.

It may, also, be noted that Kayser,¹² reports two lines, 5205.72 \AA , and 5200.41 \AA , as yttrium lines of intensity 6, while they are reported by Eder as eurosamarium lines of intensity 10.

SUMMARY

1. The arc spectrum of yttrium used for the determination of the accepted atomic weight, 89.33, was examined by means of a quartz prism.
2. Lines between the wave lengths 4526 \AA and 2330 \AA were measured and their intensities and character recorded.
3. The results found were compared with those of previous investigators.

¹¹ Sitz. K. Akad. Wiss., Wien. 126, IIa (1917), 473.

¹² *Loc. cit.*

4. The impurities present in the yttrium were holmium, erbium, dysprosium, sodium, magnesium, silicon and platinum, but all were in extremely small amounts.

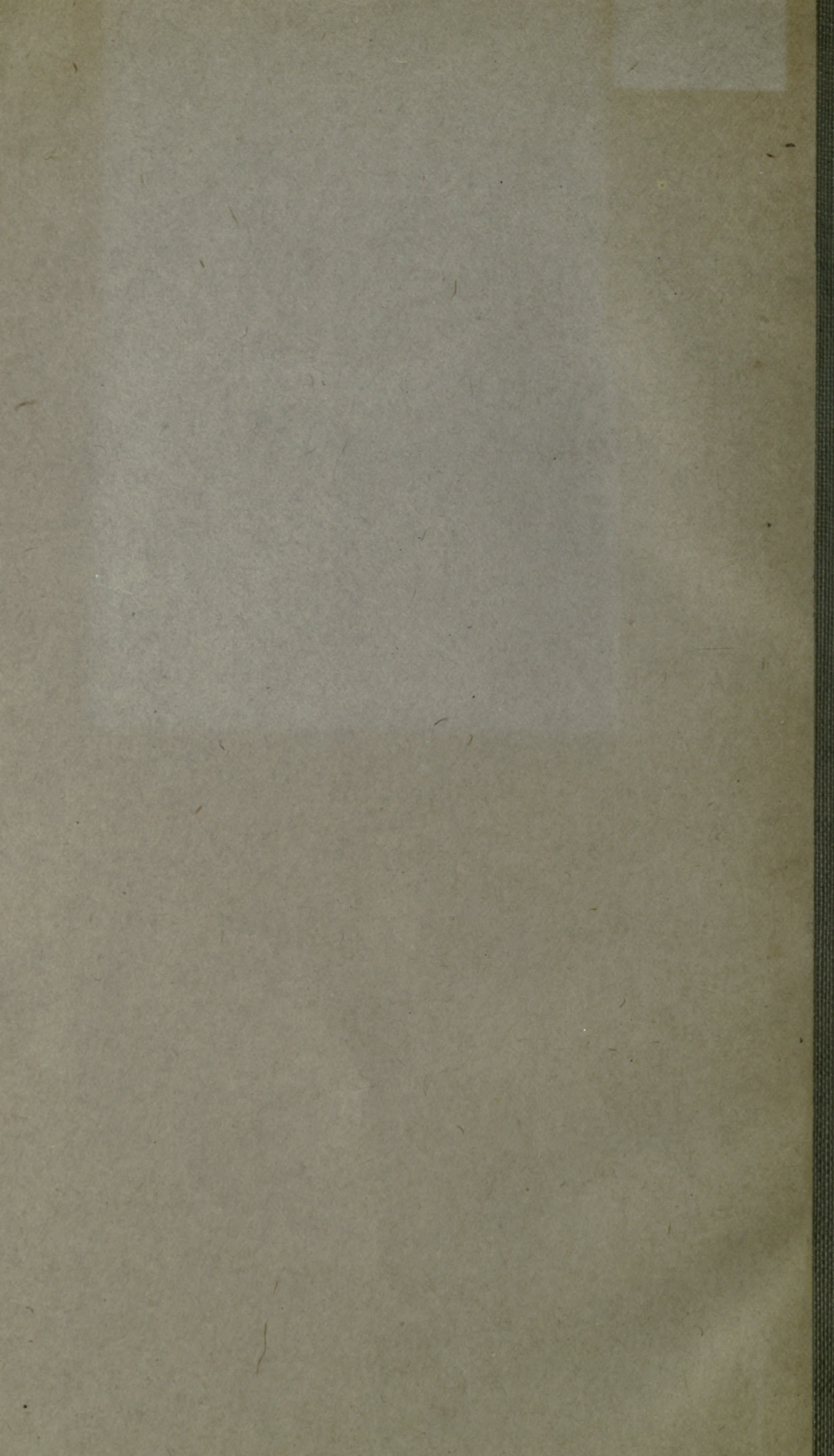
5. A number of new lines were photographed and their wave lengths determined.

URBANA, ILL.

JUNE 1, 1921.

VITA

The author was born in St. Johns, Michigan on July 29, 1892. He received his early education in the public schools of Holland Township and Holland, Michigan. He graduated from the Hope College Preparatory Department in 1911 and received the degree of A. B. from Hope College in 1915. The Graduate School of the University of Illinois granted him the degree of M. A. in Chemistry in 1917. From 1915 to 1917 and from 1919 to 1920 he held the position of Assistant in Chemistry and during the year 1920 to 1921 he was the Robert F. Carr Fellow in Chemistry at the University of Illinois.



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